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# Evaluation of two-electron integrals including the factors $r_{12}^k \exp(-\gamma r_{12}^2)$ over Cartesian Gaussian functions

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**Abstract**

We present a practical scheme for the evaluation of nonstandard two-electron integrals including the factors $r_{12}^k \exp(-\gamma r_{12}^2)$ which have been appeared recently, where $k \geqslant -1$ is an integer. The method used throughout this paper is based on the highly efficient Head-Gordon and Pople (HGP) approach of evaluation of electron repulsion integrals (ERI). Thus only straightforward modifications of existing codes that employ HGP or HGP-PRISM scheme are necessary to implement our approach.

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## 1. Introduction

Most of the standard *ab initio* methods of quantum chemistry represent the $N$-electron wave function as a linear combination of products of one-electron functions. This strong approximation leads to a very poor description of the Coulomb hole and cannot represent the electron correlation cusp in a proper way. The configuration interaction (CI) method [1] is used extensively for this purpose. The CI wave function is written as a linear combination of anti-symmetrized products of one-electron functions, and its expansion coefficients are determined by the Rayleigh–Ritz variational method. The CI method is conceptually very simple and is mathematically exact in a complete set of one-electron basis function. For obvious reasons however, the CI wave function must actually be represented in a finite one-electron basis.

To take into account the short-range correlation and thus compute very accurate atomic and molecular wave functions one must necessarily use explicitly correlated methods (for example: Hylleraas [2]). The most technically tractable of such methods employ wave functions that include explicitly the dependence on the electronic distances in a linear form, the so-called "linear $r_{12}$" methods [3].

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Several new *ab initio* methods have appeared that often yield better accuracy than available from experiment. A number of linear $r_{12}$ formulations of electron correlation methods as $R_{12}$-MP2 [4], $R_{12}$-MRCI [5] and $R_{12}$-CC [6] have appeared in the literature in combination with several types of approximations designed to remove the three- and four-electron integrals involved [7–9]. It is worth to mention the 6D potential energy surfaces for the hydrogen fluoride dimer obtained by Klopper et al. [10] within the $R_{12}$-MP2 formalism which provided results of unprecedented accuracy. Compared to other highly accurate *ab initio* approaches, linear $r_{12}$ methods, in particular $R_{12}$-MP2, are not restricted to very small chemical systems as they have been applied to molecules as large as ferrocene [11]. We can also mention the use of the geminal factor $\exp(-\gamma r_{12}^2)$ in the perturbational treatment of the correlation cusp given by Sirbu and King [12]. As an example, they have been able to obtain the helium ground state energy in error by 4 nanohartrees.

It is important to mention that the use of the linear $r_{12}$ factor for large molecules, which does not vanish for large electronic separations, yields to a wrong description of the inter-electronic interaction at least with a large separation between the electrons. Thus, an important perspective of the correlation factor $r_{12}\exp(-\gamma r_{12}^2)$ introduced by Samson et al. [13] is to be able to utilize local-correlation techniques to enforce linear scaling with respect to the molecule size. These authors have recently derived the formula within the McMurchie and Davidson [14] framework.

One can write the unnormalized primitive Cartesian Gaussian function centered at $\mathbf{A} = (A_x, A_y, A_z)^{\mathrm{T}} \in \mathbb{R}^3$ as

$$\phi_a(\mathbf{r}) = (x - A_x)^{a_x}(y - A_y)^{a_y}(z - A_z)^{z}\exp\big(-\zeta_a(\mathbf{r} - \mathbf{A})^2\big), \tag{1}$$

where $\mathbf{r} = (x, y, z)^{\mathrm{T}} \in \mathbb{R}^3$ is the coordinate vector of the electron, $\zeta_a \in ]0, \infty[$ is the orbital exponent and $\mathbf{a} = (a_x, a_y, a_z)^{\mathrm{T}} \in \mathbb{N}^3$ is a set of nonnegative integers, which is usually termed the angular momentum index. Henceforth, $a_i$ will refer to the $i$th component of $\mathbf{a}$, where $i = x, y, z$. Basic vector addition rules will apply to these triads of numbers, e.g., $\mathbf{a} + \mathbf{1}_x \equiv (a_x + 1, a_y, a_z)^{\mathrm{T}}$. The scheme presented in this paper is based on the Obara and Saika [15] (OS) method and its modification by Head-Gordon and Pople [16] (HGP) and the scheme independently introduced by Lindh, Ryu and Liu [17] and Hamilton and Schaefer [18] (which we mention by HSL) for the evaluation of the two-electron integral over Cartesian Gaussian atomic orbitals. As shown by Samson et al. [13], none of the five ERI's that arise from the use of the damped $r_{12}$ factors require much more computational time than the usual ERI calculation over GTO.

The practical scheme presented for the evaluation of the correlated integrals follows the same direction as the work by Valeev and Schaefer [19]. These authors have formulated the OS and the HGP schemes for the evaluation of the integrals over the two-particle correlation function $r_{12}$. The presence of the Gaussian factor $\exp(-\gamma r_{12}^2)$ in the current correlation function allows us to employ the properties like derivative and Cartesian factorization of the Gaussian. Thus different recurrence relations could be obtained.

## 2. Evaluation of the integrals

In Sections 2.1 and 2.2, we begin our discussion of the evaluation of the two-electron integrals by reviewing the damped-$R_{12}$ integrals that need to be evaluated and the basic spherical Gaussian integrals [13]. In Section 2.3 and 2.4 we recall the horizontal recurrence relation (HRR) and the electron transfer recurrence relation (ETRR) over any bi-electronic operators $\mathcal{O}(\mathbf{r}_1, \mathbf{r}_2)$ where $\mathbf{r}_1, \mathbf{r}_2 \in \mathbb{R}^3$ are the positions of the electrons 1 and 2, respectively. Then in Section 2.5 we give the vertical recurrence relation (VRR) which completes the set of relations needed for the evaluation of the damped-$R_{12}$ integrals. In Section 2.6 we introduce the centered bi-horizontal recurrence relation (CBHRR). The last Section 2.7 will be dedicated to the evaluation of the integral over the modified Coulomb operator $r_{12}^{-1}\exp(-\gamma r_{12}^2)$.

### 2.1. The damped-$R_{12}$ integrals

Following Samson et al. [13], the six different integrals to be considered including the correlation factor $f_{12} = r_{12}\exp(-\gamma r_{12}^2)$, where $\gamma \in [0, \infty[$ and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ the inter-electronic distance, are given by:

$$I_1 = \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_2)r_{12}^{-1}\phi_b(\mathbf{r}_1)\phi_d(\mathbf{r}_2), \tag{2}$$

$$I_2 = \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_2)r_{12}^{-1}f_{12}\phi_b(\mathbf{r}_1)\phi_d(\mathbf{r}_2), \tag{3}$$

$$I_3 = \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_2)f_{12}\phi_b(\mathbf{r}_1)\phi_d(\mathbf{r}_2), \tag{4}$$

$$I_4 = \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_2)f_{12}f'_{12}\phi_b(\mathbf{r}_1)\phi_d(\mathbf{r}_2), \tag{5}$$

$$I_5 = \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_2)[f_{12}, T_1]\phi_b(\mathbf{r}_1)\phi_d(\mathbf{r}_2), \tag{6}$$

$$I_6 = \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_2)\big[[f_{12}, T_1],\, f'_{12}\big]\phi_b(\mathbf{r}_1)\phi_d(\mathbf{r}_2), \tag{7}$$

where the $T_1$ operator is the usual kinetic-energy operator of electron 1, $[f_{12}, T_1]$ and $[[f_{12}, T_1], f'_{12}]$ are the well-known commutators which appear in $R_{12}$-theory, for flexibility in the choice of the correlation factor $f'_{12} = r_{12}\exp(-\gamma' r_{12}^2)$ has been introduced in $I_4$ and $I_6$ and the exponents $\gamma$ and $\gamma'$ are parameters. Samson et al. pointed out that the integrals involving kinetic-energy operator $I_5$ and $I_6$ can be expressed as [13,20]:

$$I_5 = \frac{1}{2}\big(\nabla_A^2 - \nabla_B^2\big)I_3, \tag{8}$$

$$I_6 = \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_2)\big(1 - 2\gamma r_{12}^2\big)\big(1 - 2\gamma' r_{12}^2\big)\exp\big(-(\gamma+\gamma')r_{12}^2\big)\phi_b(\mathbf{r}_1)\phi_d(\mathbf{r}_2). \tag{9}$$

In the following sections, we will use the short-hand notation $\mathcal{O}(\mathbf{r}_1, \mathbf{r}_2)$ for any bi-electronic operator, $\mathcal{O}_k$ for the particular operator $\mathcal{O}_k \equiv \mathcal{O}_k(\mathbf{r}_1, \mathbf{r}_2, \gamma) = r_{12}^k\exp(-\gamma r_{12}^2)$ where $k \geqslant -1$ is an integer, and the usual short hand notation for the integral

$$\big(\mathbf{ab}|\mathcal{O}(\mathbf{r}_1, \mathbf{r}_2)|\mathbf{cd}\big) = \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_2)\mathcal{O}(\mathbf{r}_1, \mathbf{r}_2)\,\phi_b(\mathbf{r}_1)\phi_d(\mathbf{r}_2). \tag{10}$$

In the subsequent sections, we will present a method for the evaluation of the integrals $(\mathbf{ab}|\mathcal{O}_k|\mathbf{cd})$ with $k = -1, 0, 1, 2, 4$, as the problem of the evaluation of the integrals (2)–(6) can be reduced to the evaluation of these "basic" integrals. We can notice that the method proposed in this paper can be generalized to any integrals over the operator $\mathcal{O}_k$ with $k \geqslant -1$.

### 2.2. Basic spherical Gaussian integrals

In this section, we summarize the evaluation of the spherical Gaussian integrals as presented in [13]. The integrals (11)–(15) can be easily evaluated

$$(\mathbf{00}|\mathcal{O}_0|\mathbf{00}) = \left(\frac{\pi^2}{\zeta_p\zeta_q}\right)^{3/2}\left(\frac{\alpha}{\alpha+\gamma}\right)^{3/2}\exp\left(-\frac{\zeta_a\zeta_b}{\zeta_p}AB^2\right)\exp\left(-\frac{\zeta_c\zeta_d}{\zeta_q}CD^2\right)\exp\left(-\frac{\alpha\gamma}{\alpha+\gamma}PQ^2\right), \tag{11}$$

$$(\mathbf{00}|\mathcal{O}_2|\mathbf{00}) = \left(\frac{3}{2}+\frac{\alpha^2}{\alpha+\gamma}PQ^2\right)\frac{(\mathbf{00}|\mathcal{O}_0|\mathbf{00})}{\alpha+\gamma}, \tag{12}$$

$$(\mathbf{00}|\mathcal{O}_4|\mathbf{00}) = \left(\frac{15}{4}+\frac{5\alpha^2}{\alpha+\gamma}PQ^2+\frac{\alpha^4}{(\alpha+\gamma)^2}PQ^4\right)\frac{(\mathbf{00}|\mathcal{O}_0|\mathbf{00})}{(\alpha+\gamma)^2}, \tag{13}$$

$$(\mathbf{00}|\mathcal{O}_{-1}|\mathbf{00}) = 2\sqrt{\frac{\alpha+\gamma}{\pi}}F_0\left(\frac{\alpha^2}{\alpha+\gamma}PQ^2\right)(\mathbf{00}|\mathcal{O}_0|\mathbf{00}), \tag{14}$$

$$(\mathbf{00}|\mathcal{O}_1|\mathbf{00}) = \left[\exp\left(-\frac{\alpha^2}{\alpha+\gamma}PQ^2\right)+\left(1+\frac{2\alpha^2}{\alpha+\gamma}PQ^2\right)F_0\left(\frac{\alpha^2}{\alpha+\gamma}PQ^2\right)\right]\frac{(\mathbf{00}|\mathcal{O}_0|\mathbf{00})}{\sqrt{\pi(\alpha+\gamma)}} \tag{15}$$

in which

$$\zeta_p = \zeta_a + \zeta_b, \tag{16}$$

$$\zeta_q = \zeta_c + \zeta_d, \tag{17}$$

$$\alpha = \frac{\zeta_p\zeta_q}{\zeta_p+\zeta_q}, \tag{18}$$

$$\mathbf{P} = \frac{\zeta_a\mathbf{A}+\zeta_b\mathbf{B}}{\zeta_p}, \tag{19}$$

$$\mathbf{Q} = \frac{\zeta_c\mathbf{C}+\zeta_d\mathbf{D}}{\zeta_q}, \tag{20}$$

$$PQ = \sqrt{PQ_x^2+PQ_y^2+PQ_z^2}, \tag{21}$$

$$PQ_i = P_i - Q_i, \quad i = x, y, z; \tag{22}$$

and where we have introduced the Boys function [1] of order $n \in \mathbb{N}$

$$F_n(z) = \int_0^1 \mathrm{d}u\, u^{2n}\exp\left(-zu^2\right). \tag{23}$$

### 2.3. Horizontal recurrence relation (HRR)

The well-known HRR introduced by Head-Gordon and Pople [16] can be generalized as

$$\left(\mathbf{ab}+\mathbf{1}_i|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{cd}\right) = \left(\mathbf{a}+\mathbf{1}_i\mathbf{b}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{cd}\right) + AB_i\left(\mathbf{ab}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{cd}\right), \tag{24}$$

which holds for any well-behaved operator $\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)$. An important feature is that the angular momentum can be transfered from the centers **A** and **C** to centers **B** and **D**, respectively, after the contraction step. It is worth to mention that numerical instability can arise during the HRR step when, for example, $\zeta_a \gg \zeta_b$ as shown by Ishida [21] for the ERI's.

### 2.4. Electron transfer recurrence relation (ETRR)

The ETRR introduced by Hamilton and Schaefer [18] and Lindh, Ryu and Liu [17] can be easily extended to any well-behaved bi-electronic operators $\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)$ as

$$\begin{aligned}\big(\mathbf{a0}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{c}+\mathbf{1}_i\mathbf{0}\big) &= \frac{1}{2\zeta_q}\big[N_i(\mathbf{a})\big(\mathbf{a}-\mathbf{1}_i\mathbf{0}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{c0}\big)+N_i(\mathbf{c})\big(\mathbf{a0}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{c}-\mathbf{1}_i\mathbf{0}\big)\big]\\ &\quad-\frac{\zeta_p}{\zeta_q}\big(\mathbf{a}+\mathbf{1}_i\mathbf{0}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{c0}\big)-\frac{\zeta_b AB_i+\zeta_d CD_i}{\zeta_q}\big(\mathbf{a0}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{c0}\big)\end{aligned}\tag{25}$$

in which, for example, $N_i(\mathbf{a})=a_i$ where $i=x,y,z$. This relation allows us to transfer the angular momentum from the second to the first electron. As in the HRR case Section 2.3, numerical instabilities can arise by the use of Eq. (25). Further discussion of the problem can be found in Ref. [21].

### 2.5. Vertical recurrence relation (VRR)

To complete the set of equations needed for the evaluation of the integrals $(\mathbf{ab}|\mathcal{O}_k|\mathbf{cd})$, we need the vertical recurrence relation for the particular bi-electronic operator $\mathcal{O}_k$. To obtain the VRR we will use the identity given by Klopper and Röhse [20]

$$\nabla_P\big(\mathbf{ab}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{cd}\big)=\big(\mathbf{ab}|\{\nabla_1\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)\}|\mathbf{cd}\big),\tag{26}$$

where $\nabla_P=\nabla_A+\nabla_B$, $\nabla_A\equiv(\frac{\partial}{\partial A_x},\frac{\partial}{\partial A_y},\frac{\partial}{\partial A_z})$, $\nabla_B\equiv(\frac{\partial}{\partial B_x},\frac{\partial}{\partial B_y},\frac{\partial}{\partial B_z})$ and finally $\nabla_1\equiv(\frac{\partial}{\partial r_{1x}},\frac{\partial}{\partial r_{1y}},\frac{\partial}{\partial r_{1z}})$. The above equality holds for integrals over any multiplicative bi-electronic operators $\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)$ if $\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_1)\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)=0$ when $|\mathbf{r}_1|\to\infty,\ \forall\mathbf{r}_2\in\mathbb{R}^3$ as shown in Appendix A.

Because we will use this in the following, we give here the $i$th component of the gradient of the operator $\mathcal{O}_k$ with respect to the electron 1:

$$\begin{aligned}[\nabla_1\mathcal{O}_k]_i &= \big[\nabla_1\big\{r_{12}^k\exp(-\gamma r_{12}^2)\big\}\big]_i=(\mathbf{r}_{12})_i\big(k-2\gamma r_{12}^2\big)r_{12}^{k-2}\exp\big(-\gamma r_{12}^2\big)\\ &=(\mathbf{r}_{12})_i(k\mathcal{O}_{k-2}-2\gamma\mathcal{O}_k),\end{aligned}\tag{27}$$

in which $(\mathbf{r}_{12})_i$ stands for $(r_{1i}-r_{2i})$. On one hand, the explicit differentiation of the left-hand side of Eq. (26) over the operators $\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)$ gives

$$\begin{aligned}\big[\nabla_P\big(\mathbf{a0}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{c0}\big)\big]_i &= \left(\frac{\partial}{\partial A_i}+\frac{\partial}{\partial B_i}\right)\big(\mathbf{a0}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{c0}\big)\\ &=2\zeta_a\big(\mathbf{a}+\mathbf{1}_i\mathbf{0}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{c0}\big)-N_i(\mathbf{a})\big(\mathbf{a}-\mathbf{1}_i\mathbf{0}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{c0}\big)\\ &\quad+2\zeta_b\big(\mathbf{a}\mathbf{1}_i|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{c0}\big)\\ &=2\zeta_p\big(\mathbf{a}+\mathbf{1}_i\mathbf{0}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{c0}\big)-N_i(\mathbf{a})\big(\mathbf{a}-\mathbf{1}_i\mathbf{0}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{c0}\big)\\ &\quad+2\zeta_b AB_i\big(\mathbf{a0}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{c0}\big),\end{aligned}\tag{28}$$

where we have used the HRR Eq. (24) to transfer a unit of angular momentum from center **B** to **A**. On the other hand, the explicit differentiation of the right-hand side of Eq. (26) with the help of Eq. (27) over the particular operator $\mathcal{O}_k$ gives

$$\begin{aligned}\big[(\mathbf{a0}|\{\nabla_1\mathcal{O}_k\}|\mathbf{c0})\big]_i &= \big(\mathbf{a0}|(\mathbf{r}_{12})_i(k\mathcal{O}_{k-2}-2\gamma\mathcal{O}_k)|\mathbf{c0}\big)=\big(\mathbf{a}+\mathbf{1}_i\mathbf{0}|(k\mathcal{O}_{k-2}-2\gamma\mathcal{O}_k)|\mathbf{c0}\big)\\ &\quad-\big(\mathbf{a0}|(k\mathcal{O}_{k-2}-2\gamma\mathcal{O}_k)|\mathbf{c}+\mathbf{1}_i\mathbf{0}\big)+AC_i\big(\mathbf{a0}|(k\mathcal{O}_{k-2}-2\gamma\mathcal{O}_k)|\mathbf{c0}\big),\end{aligned}\tag{29}$$

where we have used the fact that $(\mathbf{r}_{12})_i=(r_{1i}-A_i)-(r_{2i}-C_i)+AC_i$. Combination of Eqs. (28) and (29) gives finally an HGP-like VRR applicable to the integrals over the operator $\mathcal{O}_k$ for any integer $k\geqslant 0$

$$(\mathbf{a}+\mathbf{1}_i\mathbf{0}|\mathcal{O}_k|\mathbf{c0}) = \frac{1}{2}\frac{1}{\zeta_p\zeta_q+\gamma(\zeta_p+\zeta_q)}\big[N_i(\mathbf{a})(\zeta_q+\gamma)(\mathbf{a}-\mathbf{1}_i\mathbf{0}|\mathcal{O}_k|\mathbf{c0}) - 2\big(\zeta_b(\zeta_q+\gamma)AB_i+\gamma\zeta_d CD_i+\gamma\zeta_q AC_i\big)(\mathbf{a0}|\mathcal{O}_k|\mathbf{c0}) + \gamma N_i(\mathbf{c})(\mathbf{a0}|\mathcal{O}_k|\mathbf{c}-\mathbf{1}_i\mathbf{0}) + k\zeta_q\big\{(\mathbf{a}+\mathbf{1}_i\mathbf{0}|\mathcal{O}_{k-2}|\mathbf{c0}) - (\mathbf{a0}|\mathcal{O}_{k-2}|\mathbf{c}+\mathbf{1}_i\mathbf{0}) + AC_i(\mathbf{a0}|\mathcal{O}_{k-2}|\mathbf{c0})\big\}\big], \quad \forall k \geqslant 0. \tag{30}$$

In a similar way, it is possible to obtain an HLS-like scheme

$$(\mathbf{a}+\mathbf{1}_i\mathbf{0}|\mathcal{O}_k|\mathbf{00}) = \frac{1}{2}\frac{1}{\zeta_p\zeta_q+\gamma(\zeta_p+\zeta_q)}\big[N_i(\mathbf{a})(\zeta_q+\gamma)(\mathbf{a}-\mathbf{1}_i\mathbf{0}|\mathcal{O}_k|\mathbf{00}) - 2\big(\zeta_b(\zeta_q+\gamma)AB_i+\gamma\zeta_d CD_i+\gamma\zeta_q AC_i\big)(\mathbf{a0}|\mathcal{O}_k|\mathbf{00}) + k\zeta_q\big\{\big(\mathbf{a}+\mathbf{1}_i\mathbf{0}|\mathcal{O}_{k-2}|\mathbf{00}\big) - \big(\mathbf{a0}|\mathcal{O}_{k-2}|\mathbf{1}_i\mathbf{0}\big) + AC_i\big(\mathbf{a0}|\mathcal{O}_{k-2}|\mathbf{00}\big)\big\}\big], \quad \forall k \geqslant 0. \tag{31}$$

The special HGP case when $k = 0$ is given by

$$(\mathbf{a}+\mathbf{1}_i\mathbf{0}|\mathcal{O}_0|\mathbf{c0}) = \frac{1}{2}\frac{1}{\zeta_p\zeta_q+\gamma(\zeta_p+\zeta_q)}\big[N_i(\mathbf{a})(\zeta_q+\gamma)(\mathbf{a}-\mathbf{1}_i\mathbf{0}|\mathcal{O}_0|\mathbf{c0}) - 2\big(\zeta_b(\zeta_q+\gamma)AB_i+\gamma\zeta_d CD_i+\gamma\zeta_q AC_i\big)(\mathbf{a0}|\mathcal{O}_0|\mathbf{c0}) + \gamma N_i(\mathbf{c})(\mathbf{a0}|\mathcal{O}_0|\mathbf{c}-\mathbf{1}_i\mathbf{0})\big], \quad k = 0, \tag{32}$$

and for the HLS-like scheme

$$(\mathbf{a}+\mathbf{1}_i\mathbf{0}|\mathcal{O}_0|\mathbf{00}) = \frac{1}{2}\frac{1}{\zeta_p\zeta_q+\gamma(\zeta_p+\zeta_q)}\big[N_i(\mathbf{a})(\zeta_q+\gamma)(\mathbf{a}-\mathbf{1}_i\mathbf{0}|\mathcal{O}_0|\mathbf{00}) - 2\big(\zeta_b(\zeta_q+\gamma)AB_i+\gamma\zeta_d CD_i+\gamma\zeta_q AC_i\big)(\mathbf{a0}|\mathcal{O}_0|\mathbf{00})\big], \quad k = 0, \tag{33}$$

which are just special case of Eqs. (30) and (31), respectively.

### *2.6. Centered bi-horizontal recurrence relation (CBHRR)*

In a similar way as the HRR Section 2.3, it is possible to transfer the angular momentum from the electrons 1 and 2 to the operator $\mathcal{O}_k$. To obtain the recurrence relation we first express $r_{12}^{k+2n}$ in a trinomial expansion as

$$r_{12}^{k+2n} = r_{12}^{k}\sum_{s=0}^{n}\sum_{t=0}^{s}\binom{n}{s}\binom{s}{t}(x_1-x_2)^{2(n-s)}(y_1-y_2)^{2(s-t)}(z_1-z_2)^{2t}, \tag{34}$$

where $n \in \mathbb{N}$, an nonnegative integer. Then by the introduction of the equality

$$\begin{aligned}(r_{1i}-r_{2i})^n &= \big((r_{1i}-A_i)-(r_{2i}-C_i)+AC_i\big)^n \\ &= \sum_{u=0}^{n}\sum_{v=0}^{u}(-)^{u-v}\binom{n}{u}\binom{u}{v}(r_{1i}-A_i)^{n-u}(r_{2i}-C_i)^{u-v}AC_i^v,\end{aligned} \tag{35}$$

we obtain an expression for $r_{12}^{k+2n}$ which depends only in the difference between the position of the electron 1 or 2 and a nuclei (without looking at the multiplicative factor $r_{12}^{k}$), which writes

$$\begin{aligned}r_{12}^{k+2n} = r_{12}^{k}\sum_{s=0}^{n}\sum_{t=0}^{s}\sum_{u=0}^{2(n-s)}\sum_{v=0}^{u}\sum_{u'=0}^{2(s-t)}\sum_{v'=0}^{u'}\sum_{u''=0}^{2t}\sum_{v''=0}^{u''}(-)^{u-v+u'-v'+u''-v''} \\ \times\binom{n}{s}\binom{s}{t}\binom{2(n-s)}{u}\binom{u}{v}\binom{2(s-t)}{u'}\binom{u'}{v'}\binom{2t}{u''}\binom{u''}{v''}\end{aligned}$$

$$\times (x_1 - A_x)^{2(n-s)-u}(x_2 - C_x)^{u-v} AC_x^v$$
$$\times (y_1 - A_y)^{2(s-t)-u'}(y_2 - C_y)^{u'-v'} AC_y^{v'}$$
$$\times (z_1 - A_z)^{2t-u''}(z_2 - C_z)^{u''-v''} AC_z^{v''}. \tag{36}$$

It is then possible to write any integrals $(\mathbf{ab}|\mathcal{O}_{k+2n}|\mathbf{cd})$ as a linear combination of integrals over the operator $\mathcal{O}_k$ as

$$(\mathbf{ab}|\mathcal{O}_{k+2n}|\mathbf{cd}) = \sum_{s=0}^{n}\sum_{t=0}^{s}\sum_{u=0}^{2(n-s)}\sum_{v=0}^{u}\sum_{u'=0}^{2(s-t)}\sum_{v'=0}^{u'}\sum_{u''=0}^{2t}\sum_{v''=0}^{u''}(-)^{u-v+u'-v'+u''-v''}$$
$$\times \binom{n}{s}\binom{s}{t}\binom{2(n-s)}{u}\binom{u}{v}\binom{2(s-t)}{u'}\binom{u'}{v'}\binom{2t}{u''}\binom{u''}{v''}$$
$$\times AC_x^v AC_y^{v'} AC_z^{v''}(\tilde{\mathbf{a}}_{n,s,t,u,u',u''}\mathbf{b}|\mathcal{O}_k|\tilde{\mathbf{c}}_{u,u',u'',v,v',v''}\mathbf{d}), \tag{37}$$

where $\tilde{\mathbf{a}}_{n,s,t,u,u',u''} = \mathbf{a} + (2(n-s)-u)\mathbf{1}_x + (2(s-t)-u')\mathbf{1}_y + (2t-u'')\mathbf{1}_z$ and $\tilde{\mathbf{c}}_{u,u',u'',v,v',v''} = \mathbf{c} + (u-v)\mathbf{1}_x + (u'-v')\mathbf{1}_y + (u''-v'')\mathbf{1}_z$. When, for example, if $n = 1$ and $k = 0$ we obtain:

$$(\mathbf{ab}|\mathcal{O}_2|\mathbf{cd}) = \sum_{i=x,y,z}\big\{(\mathbf{a}+\mathbf{2}_i\mathbf{b}|\mathcal{O}_0|\mathbf{cd}) + (\mathbf{ab}|\mathcal{O}_0|\mathbf{c}+\mathbf{2}_i\mathbf{d})$$
$$- 2(\mathbf{a}+\mathbf{1}_i\mathbf{b}|\mathcal{O}_0|\mathbf{c}+\mathbf{1}_i\mathbf{d}) + 2AC_i(\mathbf{a}+\mathbf{1}_i\mathbf{b}|\mathcal{O}_0|\mathbf{cd})$$
$$- 2AC_i(\mathbf{ab}|\mathcal{O}_0|\mathbf{c}+\mathbf{1}_i\mathbf{d}) + AC_i^2(\mathbf{ab}|\mathcal{O}_0|\mathbf{cd})\big\}. \tag{38}$$

We can see that these expressions, Eq. (38) and generally Eq. (37), are very demanding especially in the second and higher cases when $2n > 2$. It is obvious that the CBHRR step can be done in the outermost contraction loop ($K^0$ loop and where $K$ is the number of contraction)[1] as the sums do not depend explicitly on the orbital exponents nor the contraction coefficients.

### *2.7. Evaluation of the integrals* $(\mathbf{ab}|\mathcal{O}_{-1}|\mathbf{cd})$

Following the same development given by Obara and Saika [15] and making the substitution $t^2 \to t^2 + \gamma$ it is then easy to obtain an Obara–Saika two-electron recurrence relation for the integral

$$(\mathbf{a}+\mathbf{1}_i\mathbf{b}|\mathcal{O}_{-1}|\mathbf{cd})^{(m)} = PA_i(\mathbf{ab}|\mathcal{O}_{-1}|\mathbf{cd})^{(m)} - \frac{\zeta_q}{\zeta_p+\zeta_q}PQ_i(\mathbf{ab}|\mathcal{O}_{-1}|\mathbf{cd})^{(m+1)}$$
$$+ \frac{1}{2}\frac{1}{\zeta_p+\zeta_q}\big[N_i(\mathbf{c})(\mathbf{ab}|\mathcal{O}_{-1}|\mathbf{c}-\mathbf{1}_i\mathbf{d})^{(m+1)} + N_i(\mathbf{d})(\mathbf{ab}|\mathcal{O}_{-1}|\mathbf{cd}-\mathbf{1}_i)^{(m+1)}\big]$$
$$+ \frac{1}{2\zeta_p}\bigg[N_i(\mathbf{a})\bigg\{(\mathbf{a}-\mathbf{1}_i\mathbf{b}|\mathcal{O}_{-1}|\mathbf{cd})^{(m)} - \frac{\alpha}{\zeta_p}(\mathbf{a}-\mathbf{1}_i\mathbf{b}|\mathcal{O}_{-1}|\mathbf{cd})^{(m+1)}\bigg\}$$
$$+ N_i(\mathbf{b})\bigg\{(\mathbf{ab}-\mathbf{1}_i|\mathcal{O}_{-1}|\mathbf{cd})^{(m)} - \frac{\alpha}{\zeta_p}(\mathbf{ab}-\mathbf{1}_i|\mathcal{O}_{-1}|\mathbf{cd})^{(m+1)}\bigg\}\bigg], \tag{39}$$

where we have used the short-hand notation

$$(\mathbf{ab}|\mathcal{O}_{-1}|\mathbf{cd})^{(m)} = \frac{2}{\sqrt{\pi}}\int_0^\infty \mathrm{d}t\left(\frac{t^2+\gamma}{\alpha+t^2+\gamma}\right)^m$$
$$\times \iint_{\mathbb{R}^3\times\mathbb{R}^3} \mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_2)\exp\big(-(t^2+\gamma)r_{12}^2\big)\phi_b(\mathbf{r}_1)\phi_d(\mathbf{r}_2), \tag{40}$$

[1] Numerical instability similar to those observed by Ishida [21], in the ERI's case, may also arise by using Eq. (37).

where $m \in \mathbb{N}$, a nonnegative integer. The use of the recurrence relation (39) requires the evaluation of the modified spherical bi-electronic integral, which is given by

$$\begin{aligned}(\mathbf{00}|\mathcal{O}_{-1}|\mathbf{00})^{(m)} &= \frac{2}{\sqrt{\pi}}\left(\frac{\pi^2}{\zeta_p\zeta_q}\right)^{3/2}\exp\left(-\frac{\zeta_a\zeta_b}{\zeta_p}AB^2\right)\exp\left(-\frac{\zeta_c\zeta_d}{\zeta_q}CD^2\right)\\ &\quad\times\int_0^\infty \mathrm{d}t\left(\frac{\alpha}{\alpha+t^2+\gamma}\right)^{3/2}\left(\frac{t^2+\gamma}{\alpha+t^2+\gamma}\right)^m\exp\left(-\frac{\alpha(t^2+\gamma)}{\alpha+t^2+\gamma}PQ^2\right)\\ &= \frac{2\pi^{5/2}}{(\alpha+\gamma)^{m+1}}\left(\frac{\alpha}{\zeta_p\zeta_q}\right)^{3/2}\exp\left(-\frac{\zeta_a\zeta_b}{\zeta_p}AB^2\right)\exp\left(-\frac{\zeta_c\zeta_d}{\zeta_q}CD^2\right)\\ &\quad\times\exp\left(-\frac{\alpha\gamma}{\alpha+\gamma}PQ^2\right)\sum_{k=0}^{m}\binom{m}{k}\alpha^k\gamma^{m-k}F_k\left(\frac{\alpha^2}{\alpha+\gamma}PQ^2\right),\end{aligned} \tag{41}$$

where the Boys function $F_n(z)$ Eq. (23) has been used. This relation can be obtained straightforwardly with the help of the variable substitution

$$u^2 = \frac{t^2}{\alpha+t^2+\gamma} \Rightarrow \mathrm{d}t = (\alpha+\gamma)^{-1}(\alpha+t^2+\gamma)^{3/2}\mathrm{d}u. \tag{42}$$

The HGP modification of Eq. (39) builds the angular momentum on centers **A** and **B**, through

$$\begin{aligned}(\mathbf{a}+\mathbf{1}_i\mathbf{0}|\mathcal{O}_{-1}|\mathbf{c0})^{(m)} &= PA_i(\mathbf{a0}|\mathcal{O}_{-1}|\mathbf{c0})^{(m)} - \frac{\zeta_q}{\zeta_p+\zeta_q}PQ_i(\mathbf{a0}|\mathcal{O}_{-1}|\mathbf{c0})^{(m+1)}\\ &\quad+\frac{1}{2}\frac{1}{\zeta_p+\zeta_q}N_i(\mathbf{c})(\mathbf{a0}|\mathcal{O}_{-1}|\mathbf{c}-\mathbf{1}_i\mathbf{0})^{(m+1)}\\ &\quad+\frac{1}{2\zeta_p}N_i(\mathbf{a})\left[(\mathbf{a}-\mathbf{1}_i\mathbf{0}|\mathcal{O}_{-1}|\mathbf{c0})^{(m)} - \frac{\alpha}{\zeta_p}(\mathbf{a}-\mathbf{1}_i\mathbf{0}|\mathcal{O}_{-1}|\mathbf{c0})^{(m+1)}\right].\end{aligned} \tag{43}$$

A similar relation can be obtained for the HLS scheme. Note that the final integral $(\mathbf{ab}|\mathcal{O}_{-1}|\mathbf{cd})^{(0)}$, when $m=0$, is equal to the desired integral $(\mathbf{ab}|\mathcal{O}_{-1}|\mathbf{cd})$. We can finally mention that the limit $\gamma \to 0$ of the integral $(\mathbf{ab}|\mathcal{O}_{-1}|\mathbf{cd})^{(m)}$ is easily obtained through Eq. (39) and the definition of the integral (40), thus

$$\lim_{\gamma\to 0}(\mathbf{ab}|\mathcal{O}_{-1}|\mathbf{cd})^{(m)} = (\mathbf{ab}|\mathbf{cd})^{(m)}, \tag{44}$$

where $(\mathbf{ab}|\mathbf{cd})^{(m)}$ is the usual modified ERI introduced in [15].

## 3. Practical aspect

From a theoretical point of view, Eqs. (43), (24), and (30) specify a complete HGP-like scheme for the evaluation of the target integrals $(\mathbf{ab}|\mathcal{O}_k|\mathbf{cd})$ with, in our case, $k=-1,0,1,2,4$. Here, we outline the approach for building the integrals within the HGP-approach, for odd $k$ we have

A-1 Apply the HGP VRR Eq. (43) to generate the integrals up to $(\mathbf{a}+\mathbf{b}+\mathbf{1}_i\mathbf{0}|\mathcal{O}_{-1}|\mathbf{c}+\mathbf{d0})$ and $(\mathbf{a}+\mathbf{b0}|\mathcal{O}_{-1}|\mathbf{c}+\mathbf{d}+\mathbf{1}_i\mathbf{0})$.
A-2 Build up the $(\mathbf{a}+\mathbf{b0}|\mathcal{O}_1|\mathbf{c}+\mathbf{d0})$ through the HGP-like VRR Eq. (30).
A-3 Use the HRR Eq. (24) to set up the target integrals $(\mathbf{ab}|\mathcal{O}_{-1}|\mathbf{cd})$ and $(\mathbf{ab}|\mathcal{O}_{-1}|\mathbf{cd})$.

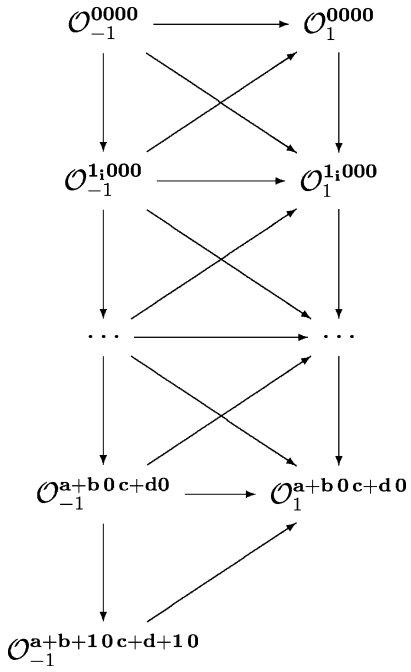


Fig. 1. Pictorial representation of the HGP vertical recurrence relation (30) applied to odd operator $\mathcal{O}_{2n-1}$ with $n = 0, 1$. The figure shows the connection, through Eq. (30), between the different intermediate integrals. The target integrals $\mathcal{O}_{2n-1}^{\mathbf{a+b0c+d0}}$ are computed in the innermost contraction loop (where we have used the short-hand notation $\mathcal{O}_{k}^{\mathbf{abcd}} \equiv (\mathbf{ab}|\mathcal{O}_k|\mathbf{cd})$).

And for the even $k$ case, we have

B-1 Apply the HGP VRR Eq. (32) to generate the integrals up to $(\mathbf{a}+\mathbf{b}+\mathbf{1}_i+\mathbf{1}_j\mathbf{0}|\mathcal{O}_0|\mathbf{c}+\mathbf{d0})$ and $(\mathbf{a}+\mathbf{b0}|\mathcal{O}_0|\mathbf{c}+\mathbf{d}+\mathbf{1}_i+\mathbf{1}_j\mathbf{0})$.
B-2 Build up the $(\mathbf{a}+\mathbf{b}+\mathbf{1}_i\mathbf{0}|\mathcal{O}_2|\mathbf{c}+\mathbf{d0})$ and $(\mathbf{a}+\mathbf{b0}|\mathcal{O}_2|\mathbf{c}+\mathbf{d}+\mathbf{1}_i\mathbf{0})$ through the HGP-like VRR Eq. (30).
B-3 Build up the $(\mathbf{a}+\mathbf{b0}|\mathcal{O}_4|\mathbf{c}+\mathbf{d0})$ through the HGP-like VRR Eq. (30).
B-4 Use the HRR Eq. (24) to set up the target integrals $(\mathbf{ab}|\mathcal{O}_0|\mathbf{cd})$, $(\mathbf{ab}|\mathcal{O}_2|\mathbf{cd})$ and $(\mathbf{ab}|\mathcal{O}_0|\mathbf{cd})$.

The steps A-3, B-3 and B-4 may be executed in the outermost contraction loop ($K^0$ loop), whereas the other steps are carried out in the innermost loop ($K^4$ loop). Pictorial representations of the HGP VRR are shown in Figs. 1 and 2 for the computation of the integrals over odd and even $k$ operators, respectively. Similar steps can be derived within the HLS frame-work (see Ref. [17]) and with the help of Eq. (31) and the HLS modification of Eq. (43). It is possible to use the CBHRR Eq. (38) if we want to evaluate the integrals $(\mathbf{ab}|\mathcal{O}_k|\mathbf{cd})$. In this case only the sufficient integrals over $\mathcal{O}_0$and $\mathcal{O}_{-1}$ must be computed in the $K^4$ loop, then the BCHRR is applied at the $K^0$ loop, after the HRR step, to give the desired integrals.

## 4. Conclusion

In this paper we propose an alternative to the McMurchie–Davidson based approach developed by Samson et al. [13] for the evaluation of the bi-electronic integrals including the factors $r_{12}^k \exp(-\gamma r_{12}^2)$. Our method is based on the Obara and Saika work and its extensions by Head-Gordon and Pople and Lindh, Ryu and Liu. It is worth

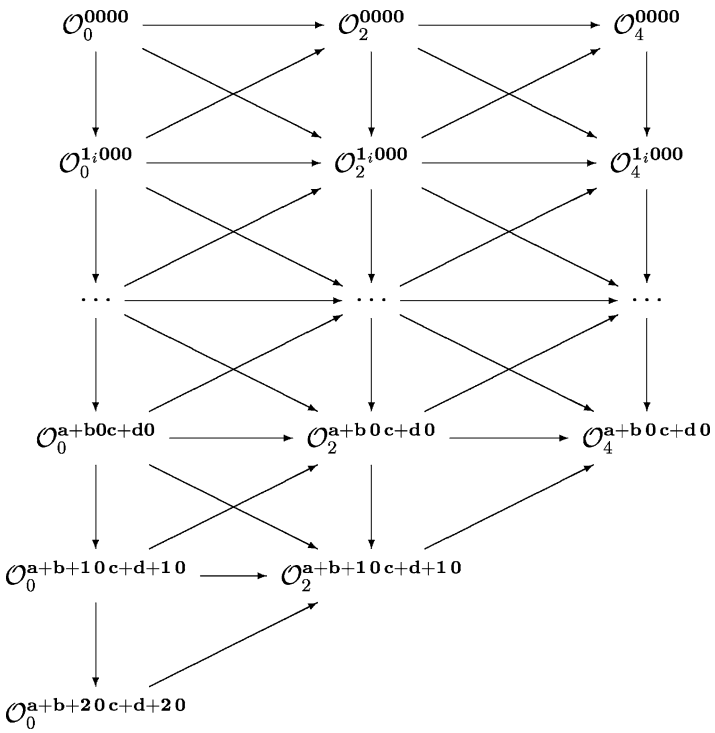


Fig. 2. Pictorial representation of the HGP VRR scheme (30) applied to even operator $\mathcal{O}_{2n}$ with $n = 0, 1, 2$. The figure shows the connection, through Eq. (30), between the different intermediate integrals. The target integrals $\mathcal{O}_{2n}^{\mathbf{a+b0c+d0}}$ are computed in the innermost contraction loop (where we have used the short-hand notation $\mathcal{O}_k^{\mathbf{abcd}} \equiv (\mathbf{ab}|\mathcal{O}_k|\mathbf{cd})$).

to mention that there are many different strategies one can devise for the implementation of these two-electron integral formulas. Moreover, it has been shown that the CBHRR can be used to transfer the angular momentum centered, for example, on **A** and **C** to the operator $\mathcal{O}_k$. Thus it is possible to compute all desired integrals over the operator $\mathcal{O}_{k+2n}$ from a set of integrals over the operator $\mathcal{O}_k$. Some questions remain about the efficiency of the methods proposed in this paper. This aspect and a comparison with the method developed by Samson et al. will be the subject of a subsequent investigation.

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## Appendix A

Eq. (26) follows from integration by parts and from the use of the equality

$$\nabla_1\{\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_1)\} = -\nabla_P\{\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_1)\},$$

which can be easily derived, then it follows

$$\begin{aligned}
\big(\mathbf{ab}|\{\nabla_1\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)\}|\mathbf{cd}\big) &= \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_2\big\{\nabla_1\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)\big\}\phi_b(\mathbf{r}_1)\phi_d(\mathbf{r}_2) \\
&= \int\limits_{\mathbb{R}^3} \mathrm{d}^3r_2\,\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_1)\phi_c(\mathbf{r}_2)\phi_d(\mathbf{r}_2)\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)\Big|_{\mathbf{r}_1=-\infty}^{\mathbf{r}_1=\infty} \\
&= \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\big\{\nabla_1\big(\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_1)\phi_c(\mathbf{r}_2)\phi_d(\mathbf{r}_2)\big)\big\}\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2) \\
&= \nabla_P \iint\limits_{\mathbb{R}^3\times\mathbb{R}^3} \mathrm{d}^3r_1\,\mathrm{d}^3r_2\,\phi_a(\mathbf{r}_1)\phi_c(\mathbf{r}_2)\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)\phi_b(\mathbf{r}_1)\phi_d(\mathbf{r}_2) \\
&= \nabla_P\big(\mathbf{ab}|\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)|\mathbf{cd}\big),
\end{aligned}$$

which holds for integrals over any well-behaved multiplicative bi-electronic operator $\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2)$ such that

$$\lim_{|\mathbf{r}_1|\to\infty} \phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_1)\mathcal{O}(\mathbf{r}_1,\mathbf{r}_2) = 0, \quad \forall\mathbf{r}_2\in\mathbb{R}^3.$$

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